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## NEWS

# Highlights from recent literature

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Each issue of *Gold Bulletin* contains key highlights from the research and patent literature. Authors who publish high-quality work in other journals are invited to send a copy of their publication to the editor for inclusion in the next issue.

## Catalysis

Selectivity of gold nanoparticles on the photocatalytic activity of TiO<sub>2</sub> for the hydroxylation of benzene by water

The influence of gold nanoparticles on the photocatalytic activity of TiO<sub>2</sub> anatase for the conversion of benzene to phenol has been studied; *Catalysis Today* (available online 10 March 2012, doi:10.1016/j.cattod.2012.01.030). Au/TiO<sub>2</sub> samples (Au loading ranging from 0.25 to 2.20 wt%) were prepared by the deposition–precipitation method and characterized by chemical analysis, TEM, XRD, and Raman spectroscopy. Photocatalytic tests revealed that the presence of gold nanoparticles initially decreases the reaction rate, but for longer reaction times, it becomes beneficial and promotes phenol formation almost doubling the reaction yield with respect to unmodified TiO<sub>2</sub>, without increasing the percentage of hydroquinone, resorcinol, and benzoquinone by-products.

A gold-catalysed enantioselective Cope rearrangement of achiral 1,5-dienes

Since the discovery of the Cope rearrangement in the 1940s, no asymmetric variant of the rearrangement of achiral 1,5-dienes has emerged, despite the successes that have been achieved with its heteroatom variants (Claisen, aza-Cope, and so on). This paper describes the first example of an enantioselective Cope reaction that starts from an achiral diene. The new gold(I) catalyst derived from double Cl<sup>−</sup>

abstraction of ((S)-3,5-xylyl-PHANEPHOS(AuCl)<sub>2</sub>) has been developed for the sigmatropic rearrangement of alkenyl methylenecyclopropanes. The reaction proceeds at low temperature, and the synthetically useful vinylcyclopropane products are obtained in high yield and enantioselectivity. Density functional theory calculations predict that: (1) the reaction proceeds via a cyclic carbenium ion intermediate, (2) the relief of strain in the methylenecyclopropane moiety provides the thermodynamic driving force for the rearrangement and (3) metal complexation of the transition-state structure lowers the rearrangement barriers. See *Nature Chemistry* 4, 405–409 (2012) doi:10.1038/nchem.1327

Au @ZrO<sub>2</sub> yolk–shell catalysts for CO oxidation: study of particle size effect by ex-post size control of Au cores

A new report in the *Journal of Catalysis* (volume 289, May 2012, pages 100–104 doi:10.1016/j.jcat.2012.01.021) describes the preparation of Au @ZrO<sub>2</sub> catalysts with gold core sizes between 5 and 15 nm by partial leaching of gold in an ex-post manner. The material obtained offers a unique comparability for particle size effect studies in CO oxidation. No effect of gold particle size was observed in the studied size range.

Formation of monometallic Au and Pd and bimetallic Au–Pd nanoparticles confined in mesopores via Ar glow-discharge plasma reduction and their catalytic applications in aerobic oxidation of benzyl alcohol

A new paper (*Journal of Catalysis*, volume 289, May 2012, pages 105–117) prepared Au–Pd bimetallic nanoparticles that were highly active in the selective oxidation of benzyl alcohol, showing a rate constant of 0.50 h<sup>−1</sup>, which was 12.5 and two times that of Au and Pd monometallic catalysts, respectively. Characterization analyses attributed the enhancement in both activity and selectivity to a Pd-rich shell/Au-rich core structure

with abundant surface coordination-unsaturated Pd atoms of those effectively confined and well-dispersed Au–Pd nanoparticles. As a green, efficient and safe protocol, plasma reduction outperformed conventional H<sub>2</sub> thermal reduction due to the different particle nucleation and growth mechanism, which afforded modified morphology and surface chemistry of metal nanoparticles. Further oxidation and re-reduction of plasma-reduced Au–Pd catalyst resulted in the atomic rearrangement of nanoparticles, leading to inferior catalytic performance.

Anisotropic growth of titania onto various gold nanostructures: synthesis, theoretical understanding, and optimization for catalysis

A facile method can tune the anisotropic growth of TiO<sub>2</sub> onto differently shaped gold nanoparticles to form Janus, eccentric, and concentric geometries according to this new paper. The Au–TiO<sub>2</sub> nanostructures were found to be energetically stable using calculations, and they possessed the highest catalytic activity out of all three geometries due to the highly accessible, exposed gold core on one side (*Angewandte Chemie International Edition* volume 50, issue 43, pages 10140–10143, October 17, 2011, doi:[10.1002/anie.201104943](https://doi.org/10.1002/anie.201104943))

Co-operative effect between copper and gold on ceria for CO-PROX reaction

In this original research article (*Catalysis Today*, volume 180, issue 1, 17 January 2012, pages 34–41), an interesting cooperative effect is shown for an Au–CuO<sub>x</sub>/CeO<sub>2</sub> catalyst: (1) moderate and totally reversible inhibition by CO<sub>2</sub> and (2) absence of inhibition by steam.

Gold nanotube membranes have catalytic properties

The authors of this paper have described the catalytic properties of gold nanotube membranes (*Microporous and Mesoporous Materials*, volume 153, 1 May 2012, pages 131–136). The work presents the fabrication of gold nanotube membranes (GNT) using gold deposition on a porous anodic aluminum oxide (AAO) template and demonstrates the catalytic properties generated by the nanostructured gold surface. AAO membranes were prepared by electrochemical anodization of Al in 0.3 M oxalic acid electrolyte. Electroless gold deposition on AAO was performed via several steps using commercially available gold plating solutions. Scanning electron microscopy images confirm that the gold nanotubes formed inside AAO pores have characteristic nanoclustered morphology as a result of the nucleation process during gold deposition. It was found that catalytic properties of GNT membranes depend on the size of gold nanoclusters which can be controlled by pH during nucleation process. The excellent catalytic properties (catalytic rate constant  $k=0.132\text{ min}^{-1}$ ) of the GNT membranes were

demonstrated by testing catalytic conversion of 4-nitrophenol into 4-aminophenol in the presence of NaBH<sub>4</sub> as a reductant. The correlation between the size of gold nanoclusters and catalytic activity was verified showing the capability of controlling and further improving catalytic properties of GNT membranes.

Gold catalysis: effect of particle size on reactivity towards various substrates

In this contribution (*Catalysis Today* volume 181, issue 1, 12 February 2012, pages 26–32), the general rules and the exceptions in the area of gold catalysis are discussed in order to establish a correlation between the size of the catalytically active element and its reactivity towards different classes of substrate molecules. The general behaviour of gold is that it is inactive in massive form while it can be used as a highly active catalyst when downsized. Throughout this paper experimental data from different sources are collected to prove that—according to this general behaviour—small molecules (CO, NO, etc.) can be activated only on small nanoparticles or roughened Au(111) surfaces, whereas Au (111) single crystals or extended metal films are active in the reaction of large molecules. This observation defines the applicability area of gold nanoparticles and the activity of large gold surfaces, films or single crystals.

## Electronics

Observations of IMC formation for Au wire bonds to Al pads

Wire bonding remains one of the most important industrial uses of gold. In this new research (*Journal of Electronic Materials*, volume 41, number 4, 748–756, doi:[10.1007/s11664-011-1805-8](https://doi.org/10.1007/s11664-011-1805-8)), a study of intermetallic compound formation has been undertaken. The investigation of Au wire bonds to Al pads revealed the evolution of a multiphase system whose terminal phases depended on the composition of the Au wire. Scanning transmission electron microscopy/energy-dispersive spectroscopy and electron diffraction data are presented for Au/Al wire bonds using both Pd-doped, 99 % pure Au wire (2N) and 99.99 % pure Au wire (4N) in the as-formed state, upon completion of overmold operations, and after reflow and aging. The reacted interfaces of both the 2N and 4N bonds were found to take on a bilayer intermetallic compound (IMC) microstructure that persisted with aging and phase changes; it is the interface of this bilayer that is believed to be susceptible to mechanical degradation. Pd was found to accumulate in the IMC near the Au/IMC interface for 2N wire

bonds and appears to lead to a phase evolution different from that for 4N wire that may be responsible for enhanced reliability of the 2N wire bond with high-temperature aging.

Evaluation of corrosion resistance and cytotoxicity of electrodeposited gold on various types of intermediate layers

Gold-plated surfaces are widely applied in several applications including electronics. The authors of this paper in *Surface Engineering* (volume 28, number 2, March 2012, pp. 108–112(5)) describe how two main issues regarding the discussion on the field of precious metal coatings concern the increase in the use of thinner gold layers and ‘Ni-free’ substrates. In order to ensure the quality of the final products, the effects of the plated surfaces on their performance require thorough and accurate research. In this paper, the corrosion resistance of gold plated nickel, copper and bronze was investigated by electrochemical methods specifically potentiodynamic polarisation and electrochemical impedance spectroscopy in phosphate-buffered saline. The cytotoxicity of the gold-plated substrates was also evaluated and compared. The results showed that the substrate related to the best corrosion resistance and cytotoxicity among the tested ones was bronze, and the one with the lowest performance was nickel.

## Nanotechnology

Formation of bamboo-like conducting carbon nanotubes decorated with Au nanoparticles by the thermal decomposition of sucrose in an AAO template

This paper (*Carbon*, volume 50, issue 7, June 2012, pages 2465–2471) from a team at Pukyong National University describes an easy method for the preparation of bamboo-like conducting carbon nanotubes decorated with Au nanoparticles (Au-CNT). The technique involves carbonization of sucrose inside of anodic aluminum oxide (AAO) nanochannels (~80 nm and ~30  $\mu\text{m}$  in diameter and length, respectively). First, the AAO membrane nanochannels were coated with Au nanoparticles (~10 nm in diameter) and the carbon nanotubes were then formed in the same channels below 973 K. Electron microscopy showed long bamboo-like carbon nanotubes, ~30  $\mu\text{m}$  in length, decorated with crystalline gold nanoparticles, ~50 nm in diameter. The coalescence of the precoated small Au nanoparticles inside the channel resulted in the attached large Au nanoparticles. The apparent resistivity of the Au-CNT prepared at 973 K was ~16.8  $\Omega\text{ cm}$ .

Surface plasmon mapping of dumbbell-shaped gold nanorods: the effect of silver coating

The authors report on the identification of surface plasmons in individual gold dumbbell-shaped nanoparticles (AuDBs), as well as AuDBs coated with silver (*Langmuir*, doi:10.1021/la300269n). They used spatially resolved electron energy loss spectroscopy in a scanning electron microscope, which allowed them to map plasmon energy and intensity spatial distributions. Two dominant plasmon resonances are experimentally resolved in both AuDBs and silver-coated AuDBs. The intensity of these features is peaked either at the tips or at the sides of the nanoparticles. The authors present boundary element method simulations in good agreement with the experiment, allowing them to elucidate the nature of such modes. While the lower-energy, tip-focused plasmon is of longitudinal character for all dumbbells under consideration, the second side-bound plasmon has a more involved symmetry, starting as a longitudinal quadrupole in homogeneous AuDBs and picking up transversal components when silver coating is added. The longitudinal dipolar mode energy is found to blue shift upon coating with silver. The paper finds that the substrate produces sizeable shifts in the plasmons of silver-coated AuDBs. Analysis portrays a complex plasmonic scenario in metal nanoparticles coated with silver, including a transition from the original homogeneous gold dumbbell plasmons to the modes of homogeneous silver rods. The authors believe that these findings can have potential application to plasmon engineering.

Direct surface plasmon induced reduction of metal salts

In this communication (*Electrochemistry Communications*, volume 17, April 2012, pages 96–99, doi:10.1016/j.elecom.2012.01.017), the authors report that the surface plasmon induced reduction of metal salts wherein the ‘hot holes’ generated during the surface plasmon resonance of gold nanoparticles are indirectly used to reduce metal ions by a citrate oxidation step. They show the reduction process of two metals, namely silver and copper by exciting the gold nanoparticles with 589 and 658 nm light source at room temperature, thus highlighting the possibility of reducing metal salts by plasmon-mediated technique.

Au–Ag nanoparticles as red pigment in ceramic inks for digital decoration

Novel pigments, consisting of Au–Ag-mixed nanoparticles, were developed for digital decoration by ink jet printing of ceramic wares. Special attention was paid to set up a microwave-assisted synthesis route, with a low environmental impact, easily transferable to large-scale production.

Several suspensions, based on Au, Ag and Au–Ag-mixed nanoparticles were prepared, trying to get a core–shell assemblage, and the synthesis parameters like metal concentration, Ag/Au ratio, time, temperature and chelating agent amount were optimized. The suspensions are stable over many months, and a total reaction yield, assessed by ICP-AES analysis, was achieved. Particle size, shape, composition and optical properties were measured by DLS, TEM-EDS, XRD and UV–Vis spectroscopy. The prepared inks were applied on ceramic tiles simulating the ceramic process, and the colour performance, assessed by colourimetry, was expressed in the CIELab parameters. This work is published in *Dyes and Pigments*, volume 94, issue 2, August 2012, pages 355–362.

Starfruit-shaped gold nanorods and nanowires: synthesis and SERS characterization

This online first article published in *Langmuir* doi:[10.1021/la300218z](https://doi.org/10.1021/la300218z) describes the first examples of higher-order penta-branched gold particles including rod-, wire-, and plate-like particles which contain a uniquely periodic starfruit-like morphology. These nanoparticles were synthesized in the presence of silver ions by a seed-mediated approach based on utilizing highly purified pentahedrally twinned gold nanorods and nanowires as seed particles. The extent of the growth can be varied, leading to shifts in the plasmon resonances of the particles. In addition, the application of the starfruit rods for surface-enhanced Raman spectroscopy is demonstrated by the authors.

Protein adsorption on gold nanoparticles supported by a layered double hydroxide

In this *Materials Letters* paper (doi:[10.1016/j.matlet.2012.02.121](https://doi.org/10.1016/j.matlet.2012.02.121)) a composite of gold nanoparticles loaded on a layered double hydroxide (AuNPs-LDH) was prepared by in situ reduction method, and its adsorption for hemoglobin (Hb), bovine serum albumin (BSA), and lysozyme (LYZ) were investigated. The results show that AuNPs-LDH composite exhibits the different adsorption capacities, and a significantly higher adsorption for Hb was observed. The effects of concentration, pH, and ionic strength of the protein solution on adsorption were examined. The pseudo-second-order kinetic model was used to simulate the adsorption process of Hb onto the AuNPs-LDH composite. Furthermore, the AuNPs-LDH composite does not deactivate during the adsorption process, and can be easily separated from the reaction system. The results indicate that AuNPs-LDH can be used as an attractive regenerative and recyclable adsorbent for protein.

Gold nanostars: surfactant-free synthesis, 3D modelling, and two-photon photoluminescence imaging

Understanding the control of the optical and plasmonic properties of gold nanostars could allow superior design and fabrication for biomedical applications. In this paper (*Nanotechnology*, volume 23, number 7, 24 February 2012, pp. 75102–75110(9)), the authors present a new, surfactant-free synthesis method of biocompatible gold nanostars with adjustable geometry such that the plasmon band can be tuned into the near-infrared region ‘tissue diagnostic window’, which is most suitable for in vivo imaging. Theoretical modelling was performed for multiple-branched 3D nanostars and yielded absorption spectra in good agreement with experimental results. The plasmon band shift was attributed to variations in branch aspect ratio, and the plasmon band intensifies with increasing branch number, branch length, and overall star size. Nanostars showed an extremely strong two-photon photoluminescence (TPL) process. The TPL imaging of wheat-germ agglutinin (WGA) functionalized nanostars on BT549 breast cancer cells and of PEGylated nanostars circulating in the vasculature, examined through a dorsal window chamber in vivo in laboratory mouse studies, demonstrated that gold nanostars can serve as an efficient contrast agent for biological imaging applications.

3D micro-structures by piezoelectric inkjet printing of gold nanofluids

3D solid and pocketed micro-wires and micro-walls are needed for emerging applications that require fine-scale functional structures in three dimensions, including micro-heaters, micro-reactors and solar cells. To fulfill this demand, 3D microstructures with high aspect ratios (>50:1) are developed on a low-cost basis that is applicable for mass production with high throughput, also enabling the printing of structures that cannot be manufactured by conventional techniques. Additively patterned 3D gold micro-walls and -wires are grown by piezoelectric inkjet printing of nanofluids, selectively combined with in situ simultaneous laser annealing that can be applied to large-scale bulk production. It is demonstrated how the results of 3D printing depend on the piezoelectric voltage pulse, the substrate heating temperature and the structure height, resulting in the identification of thermal regions of optimal printing for best printing results. Furthermore a parametric analysis of the applied substrate temperature during printing leads to proposed temperature ranges for solid and pocketed micro-wire and micro-wall growth for selected frequency and voltages. See *Journal of Micromechanics and Microengineering*, volume 22, number 5 for more information.



## Recycling

### Recovery of gold from secondary sources—a review

*Hydrometallurgy* (volumes 115–116, March 2012, pages 30–51) has published an overview of the various methodologies used in the recovery of gold from secondary sources, e.g. waste electronics. The state of art in recovery of gold from spent sources by pyrometallurgy, hydrometallurgy, and bio-hydrometallurgy techniques is highlighted in this paper. This article also provides an overview of past achievements and present scenario of recovery studies carried out on the use of some promising methods which could serve as an economical means for recovering gold. The present review also highlights the used varieties of leaching, cementing, reducing agents, peeling, coagulants, adsorbents, agglomeration solvents, ion exchange resins and bio-sorbents in real situations and hopes to provide insights into recovery of gold from spent sources. Evaluation of lucrative and environmentally friendly technologies to recover gold from primary and secondary spent sources was made in this study.

## Sensors

### Fluorophore–gold nanoparticle complex for sensitive optical biosensing and imaging

A paper in *Nanotechnology*, volume 23, number 9, 9 March 2012, pp. 95501–95513(13) describes how fluorophores have been extensively used as the signal mediator in biosensing and bio-imaging for a long time. In this study, the effects of these parameters on the fluorescence enhancement of commonly used fluorophores by gold nanoparticles (GNPs) are theoretically analyzed. Experimentally, an NIR contrast agent with enhanced fluorescence was developed by carefully tailoring the distance between Cypate (ICG-based fluorophore) and a GNP, via biocompatible spacer constructs. The effect of the GNP size (3.7–16.4 nm) and spacer length (3.2–4.6 nm) on fluorescence enhancement was studied, and the spacer length that provided the significant enhancement was determined. The spacer of 3.9 nm with 16.4 nm GNP provided the fluorescence of 360 % of the control. The experimental data qualitatively agreed with the theoretical results, and thus, the theoretical analysis can be used as a guide for significantly improving the sensitivity of existing fluorescent contrast agents by properly utilizing GNPs and spacers.

### Gold nanoparticle sensor for the visual detection of pork adulteration in meatball formulation

This special issue of the *Journal of Nanomaterials* on nanocrystals for electronic and optoelectronic applications (volume

2012, January 2012, doi:[10.1155/2012/103607](https://doi.org/10.1155/2012/103607)) reports on the detection of pork adulteration in beef and chicken meatball preparations using 20 nm gold nanoparticles as colorimetric sensors. In certain markets, verification of pork adulteration is necessary to meet the Halal and Kosher food standards. This label-free, low-cost assay could find applications in food analysis and genetic screening in the future.

### Enhancing surface plasmon detection using template-stripped gold nanoslit arrays on plastic films

In this new paper published online, *ACS Nano* (doi:[10.1021/nl3001142](https://doi.org/10.1021/nl3001142)), a new nanosensor is proposed. The authors explain how nanostructure-based sensors are capable of sensitive and label-free detections for biomedical applications. However, high-throughput and low-cost fabrication is the main issue which needs to be addressed. In this study, chip-based nanostructures for intensity-sensitive detection were fabricated and tested using a thermal annealing-assisted template stripping method. Large-area uniform nanoslit arrays with 500 nm period and various slit widths, from 30 to 165 nm, were made on plastic films. A transverse magnetic polarized wave in these gold nanostructures generated sharp and asymmetric Fano resonances in transmission spectra. The full width at half maximum bandwidth decreased with the decrease of slit width. The narrowest bandwidth was smaller than 10 nm. Compared to nanoslit arrays using electron beam lithography on glass substrates, the proposed chip has a higher intensity sensitivity up to 10,367 %/refractive index unit and reaches a figure of merit up to 55. The higher intensity sensitivity for the template-stripped nanostructure is attributed to smoother gold surface and larger grain size on plastic film, which reduces the surface plasmon propagation loss.

## Fuel cells

### The characteristics and performance of electroless nickel and immersion Au plated aluminum alloy bipolar plates in polymer electrolyte membrane fuel cells

There is currently a great deal of interest in finding cheap, lightweight, and malleable materials for fuel cell bipolar plates. Al alloy 5052 is suggested as one such material in proton exchange membrane fuel cells. This work presents the first research in producing Au/Ni–P multilayer coatings on Al–alloy BPPs using an electroless Ni–P along with immersion gold techniques. The modified Al–alloy BPPs were investigated to evaluate the coating structure, corrosion resistance, interfacial contact resistance, electrochemical impedance of single cells, and single-cell performance.

The results indicated that the Al–alloy BPPs with Au/Ni–P coatings, in which Ni–P is prepared at pH 4.5, reveal the lowest contact resistance and the best corrosion resistance ( $I_{\text{corr}}=8.43 \times 10^{-6} \text{ A cm}^{-2}$ ) in a 0.5 M  $\text{H}_2\text{SO}_4$ +2 ppm HF solution among all of the modified specimens. This work is published in the *Journal of Power Sources* and available online doi:[10.1016/j.jpowsour.2012.04.030](https://doi.org/10.1016/j.jpowsour.2012.04.030)

## Decoration

Dorure, décor et sublimation de la matière (Gilding, a sublimated decoration of matter)

A book, by Evelyne Darque-Ceretti and Marc Aucouturier, devoted to gilding has been recently published by the Presses des Mines in Paris (<http://www.pressesdesmines.com/science-de-la-matiere/dorure.html>). The small book (160 pages), written in French, develops an overview for

non-specialised post-graduate students and/or teachers on the history and process evolution of gilding on all kind of materials, metal, ceramic, glass, wood, cartonage, paper, etc. Particular attention is given on the mechanical modelling of gold leaf production with a thickness down to a fraction of micrometres, on the innumerable gilding recipes described in the historical and modern literature, on the structural, physical and chemical properties of the gold–substrate interface and on the complicated and difficult problem of choosing an adhesive matter to obtain a durable gilding decoration. The authors are senior researchers specialising in materials surface science and its application to cultural heritage and industrial items.

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